

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 July 2002 (04.07.2002)

PCT

(10) International Publication Number
WO 02/052347 A1

(51) International Patent Classification⁷: **G03F 7/20**

(21) International Application Number: PCT/US00/35394

(22) International Filing Date:
21 December 2000 (21.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **EUV LIMITED LIABILITY CORPORATION** [US/US];
2200 Mission College Boulevard, Mail Stop SCI-02, Santa Clara, CA 95052 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KLEBANOFF, Leonard, E.** [US/US]; 7397 Hansen Drive, Dublin, CA 94568 (US). **STULEN, Richard, H.** [US/US]; 2636 Chardonnay Way, Livermore, CA 94550 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(74) Agent: **JEW, Charles, H.**; Burns, Doane, Swecker & Mathis, LLP, P.O. Box 1404, Alexandria, VA 22314-1404 (US).

(54) Title: MITIGATION OF RADIATION INDUCED SURFACE CONTAMINATION

(57) Abstract: A process for mitigating or eliminating contamination and/or degradation of surfaces having common, adventitious atmospheric contaminants adsorbed thereon and exposed to radiation. A gas or a mixture of gases is introduced into the environment of a surface(s) to be protected. The choice of the gaseous species to be introduced (typically a hydrocarbon gas, water vapor, or oxygen or mixtures thereof) is dependent upon the contaminant as well as the ability of the gaseous species to bind to the surface to be protected. When the surface and associated bound species are exposed to radiation reactive species are formed that react with surface contaminants such as carbon or oxide films to form volatile products (e.g., CO, CO₂) which desorb from the surface.

MITIGATION OF RADIATION INDUCED SURFACE CONTAMINATION

5

BACKGROUND OF THE INVENTION

The present invention is directed generally to a process for mitigating degradation and contamination of surfaces caused by radiation induced breakdown of molecules and their subsequent reaction and/or deposition on these surfaces. More particularly, the process disclosed herein is directed to protection of the surfaces of components of a lithographic stepper, such as the mask and imaging optics, from the consequences of radiation induced molecular breakdown.

Photolithography is a well-known technique for applying patterns to the surface of a workpiece, such as a circuit pattern to a semiconductor chip or wafer. This technique has the advantage of being able to faithfully reproduce small and intricate patterns. Traditional photolithography involves applying electromagnetic radiation to a mask having openings formed therein (transmission mask) such that the light or radiation that passes through the openings is applied to a region on the surface of the workpiece that is coated with a radiation-sensitive substance, e.g., a photoresist. The mask pattern is reproduced on the surface of the workpiece by removing the exposed or unexposed photoresist. However, the capabilities of conventional photolithographic techniques have been severely challenged by the need for circuitry of increasing density and higher resolution features. The demand for smaller feature sizes has inexorably driven the wavelength of radiation needed to produce the desired pattern to ever-shorter wavelengths. As the wavelength of the applied radiation is made shorter the energy of the radiation becomes greater to the point where the radiation can cause the decomposition of

molecules adsorbed on or proximate to a surface to produce reactive species that can attack, degrade, or otherwise contaminate the surface.

While short wavelength radiation can directly dissociate molecules, secondary electrons, created by the interaction of this radiation with surfaces, are the primary agents for molecular dissociation. Low energy (5-10 eV) secondary electrons are known to be very active in breaking chemical bonds by direct ionization of adsorbed molecules or by electron attachment, wherein a secondary electron binds to a molecule producing a reactive negative ion that then de-excites to a dissociated product. Any type of radiation (photons, electrons, ions, and particles) that is energetic enough to liberate electrons can create secondary electrons; typically, energies of about 4-5 eV are required. Consequently, radiation induced contamination, i.e., contamination of surfaces by reactive species produced by secondary electrons originating from radiative interactions, will most certainly occur in lithographic processes that use energetic radiation such as: extreme ultraviolet lithography (photon energy of about 100eV), projection electron lithography (electron energy of about 50-100 keV), ion beam lithography (ion energy >10keV), 193 nm lithography (photon energy of about 6.4 eV) and 157 nm lithography (photon energy of about 7.9 eV). Thus, the potential for contamination of critical lithographic components, such as masks and optical surfaces, and degradation of their operational capability is present in all the advanced lithographic processes.

A mechanism for the contamination of surfaces having gaseous species adsorbed thereon and exposed to an incident flux of radiation is illustrated schematically in Fig. 1. Here, surface 110 has both hydrocarbon and water molecules adsorbed thereon. The term "hydrocarbon" can include any carbon containing species. Exposure to a radiation flux causes secondary electrons to be emitted from surface 110 that can dissociate the adsorbed hydrocarbon molecules to form reactive carbon fragments that can form a graphite layer on

the surface. By way of example, exposure of a Si-terminated Mo/Si multilayer mirror to a flux density of about 330 mW/mm² of 13.4 nm radiation at a background pressure of 1x10⁻⁷ Torr for about 45 hours results in the growth of a layer of graphitic carbon having a thickness of about 230 Å. The graphitic carbon film, produced by the secondary-electron-induced dissociation of hydrocarbon molecules adsorbed on the surface from this environment reduced mirror reflectivity from 66% to 12%, a loss in reflectivity that would render the multilayer mirror inoperable in a lithographic stepper.

Similarly, secondary electrons emitted from surface 110 in response to the radiation flux can dissociate adsorbed water molecules to form reactive oxygen species that can oxidize a surface to form an oxide film that can degrade the reflectivity of a mirror by absorption of radiation. Thus, oxidation resulting from radiation induced dissociation of water molecules can catastrophically and irreversibly damage optical surfaces. By way of example, exposure of a Si-terminated Mo/Si multilayer mirror to a flux density of about 330 mW/mm² of 13.4 nm radiation and 1x10⁻⁷ Torr of water vapor for about 24 hours results in the growth of a layer of SiO₂. This SiO₂ layer, which cannot be removed without damaging the Mo/Si multilayer structure, caused reflectivity to be reduced from 66% to 59%, a result that is unacceptable for operational purposes.

Accordingly, what is required is a process for eliminating or significantly mitigating contamination and/or degradation of surfaces, and particularly surfaces of critical lithographic components, exposed to radiation in the presence of common contaminants such as hydrocarbons and water vapor. This is especially true for the emerging lithographic processes that use shorter wavelength and thus higher energy radiation because of the significant potential for degrading critical components and the extreme sensitivity of these

components to small changes in surface properties.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for mitigating or eliminating contamination of surfaces by common, adventitious atmospheric molecular compounds dissociated by exposure to a radiative flux.

It is a further object to provide a process that operates effectively at sub-atmospheric pressures.

In the inventive process disclosed herein a gas or a mixture of gases is introduced into the environment of a surface(s) to be protected. The choice of the gaseous species to be introduced is dependent upon the contamination as well as the ability of the gaseous species to bind to the surface to be protected. The latter criterion is invoked so that secondary electrons emitted from the surface in response to incident radiation can dissociate the adsorbed species. When the surface and associated bound species are exposed to radiation, reactive species are formed that react with surface contaminants such as carbon or oxide films to form volatile products (e.g., CO, CO₂) which desorb from the surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates schematically a process resulting in surface contamination.

Figure 2 illustrates schematically an embodiment of the present invention.

Figure 3A depicts the oxidation of a Si surface exposed to electron beam irradiation and water vapor.

Figure 3B shows mitigation of oxidation caused by the addition of ethanol.

Figure 4 shows the effect of water vapor and ethanol on a Si surface exposed to EUV radiation.

Figure 5 shows the effect of molecular oxygen on carbon deposition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for mitigating or eliminating contamination and/or degradation of surfaces having common, adventitious atmospheric contaminants adsorbed thereon and exposed to energetic radiation. These contaminants can include such species as hydrocarbons and water vapor that can be inherently present in the atmosphere of any system and generally can arise from such sources as materials of construction, vacuum pump oils and greases. Energetic radiation can be photons, electrons, or ions. This invention finds particular utility in those lithographic processes that employ highly energetic radiation such as extreme ultraviolet radiation and thus present a significant potential for contamination and, as a consequence, degradation of the performance of critical components.

While the process of the present invention is illustrated by application to extreme ultraviolet (EUV) lithography, and particularly to the mitigation of two common forms of contamination prevalent therein, carbon deposition and oxidation, its use is not limited to lithographic operations or elimination of carbon deposition or oxidation but is contemplated to be applicable generally.

The process of the present invention is illustrated and explained by reference to Fig. 2, which shows a Si surface 210 of a Mo/Si multilayer mirror. Generally, water vapor will be present in any system, particularly an unbaked vacuum system. Thus, adventitious water vapor arises from outgassing of various system components and these water vapor molecules can be adsorbed onto any surface, such as illustrated by Fig. 2. Subjecting surface 210 to high energy radiation, such as by EUV radiation, can cause secondary electrons to be ejected from surface 210. As discussed above, these electrons can react with the adsorbed water molecules causing them to dissociate into reactive oxygen species that will, in turn, react with the Si surface. Prior to exposing surface

210 to incident radiation a small amount of a hydrocarbon gas that will also bind to surface 210 is admitted to the system. In the example illustrated by Fig. 2, the hydrocarbon gas is ethanol (C_2H_5OH). As was the case with bound water vapor, C_2H_5OH molecules bound to surface 210 will also be dissociated by the secondary electrons ejected from that surface. Reactive carbon fragments from the dissociated C_2H_5OH can react with reactive oxygen species on surface 210 to form volatile products such as CO and CO_2 . In this way reactive oxygen species that could oxidize the Si surface and degrade its reflectivity are eliminated.

It will be appreciated that the process described above can function in the opposite manner. That is, when an environment is rich in carbon containing gases carbon contamination of surfaces can be produced by radiation exposure and the primary surface contaminant can be graphitic carbon. As discussed above, the presence of graphitic carbon on mirror surfaces can cause drastic reductions in their reflectivity for EUV radiation. Therefore, in these cases it is advantageous to admit an oxygen containing gas into the environment, such as water vapor or molecular oxygen. By substituting water vapor or molecular oxygen for a hydrocarbon gas, the same process as discussed above and illustrated in Fig. 2 can remove carbon contamination as carbon oxides (CO and CO_2).

A demonstration of the ability of the novel process described herein to eliminate surface contamination caused by exposure of adventitious molecular species to high energy radiation is given by the following examples.

EXAMPLE 1

Initially, a Si-terminated multilayer mirror was exposed to an electron beam current density of about $5 \mu A/mm^2$ at a beam energy of 2 keV in the presence of about 2×10^{-7} Torr of water vapor. The chemical composition of the

surface of the mirror was monitored as a function of time. The Auger peak heights (which reflect the surface composition) of Si and SiO₂ are shown in Fig. 3A. It can be seen that the composition of the surface changed rapidly from Si to SiO₂ as oxidation progressed with a corresponding degradation in reflectivity.

The experiment above was repeated except that about 4×10^{-7} Torr of ethanol was added to the 2×10^{-7} Torr of water vapor the environment contained. As before, the chemical composition of the surface of the mirror was monitored as a function of time and the results are shown in Fig. 3B. It can be seen that, in contrast to the case where only water vapor was present, there is only a very small amount of SiO₂ present on the Si mirror surface; an amount consistent with the native oxide film typically found on Si. Further, post exposure analysis of the surface of the exposed mirror surface showed the presence of a film of graphitic carbon about 5 Å thick.

It is the presence of a native oxide film on Si that determines the choice of the gas phase molecules used to protect against surface contamination. Recalling that one important prerequisite for the choice of gas phase molecules is that these molecules must first bind to the surface to be protected so that dissociation by secondary electron emission can take place, thereby liberating reactive species on the surface itself. Consequently, the preferred hydrocarbon molecules are those that will bind to native surface constituents, for example, a polar, hydroxylated film such as can be found on the surfaces of glasses, metals, and silicon. Therefore, hydrocarbon molecules containing such polar functional groups as ketones, aldehydes, esters, alcohols, amines, thiols, and carboxylic acids that will bind well to hydroxylated surfaces are preferred. It has been shown that non-hydrogen bonding hydrogen molecules, such as ethane, cannot confer any protection from oxidation to Si surfaces, presumably because

these non-polar molecules cannot bind to the Si surface, and by analogy to any hydroxylated surface. Moreover, because the sticking coefficients for both ethanol and water vapor on a graphitic carbon surface are very small the growth of the graphitic carbon film produced when ethanol was used to provide oxidation protection tends to be self-limiting to a thickness of about 5 Å. Thus, the use of ethanol cannot lead to the formation of a catastrophically thick carbon layer, which itself would be undesirable. The self-limiting behavior leads to a large process latitude for the prevention method.

EXAMPLE 2

10 A Si-terminated Mo/Si mirror was exposed to 13.4 nm EUV radiation at a power level of about 7 mW/mm². The mirror was exposed to four different exposure conditions and the secondary electron emission was plotted as a function of time in Fig. 4. The exposure conditions were: background pressure (about 4×10^{-9} Torr); ethanol alone at a pressure of 4×10^{-7} Torr; water vapor
15 alone at a pressure of 2×10^{-7} Torr; and a mixture of ethanol (4×10^{-7} Torr) and water vapor (2×10^{-7} Torr). Secondary electron emission has been shown to be a useful monitor of the surface processes because the onset of oxidation is signaled by a very rapid increase in secondary electron emission that is due to EUV absorption by oxygen with subsequent emission of secondary electrons.
20 On the other hand, carbon deposition is signaled by a decrease in secondary electron emission due to the poor secondary electron emission characteristics of carbon.

Referring now to Fig. 4, it can be seen that exposure of the Si surface to water vapor in the presence of EUV radiation is accompanied by a rapid
25 increase in the secondary electron signal denoting the formation of an oxide film. However, when ethanol is admitted the increase in secondary electron

signal attributable to surface oxidation is significantly reduced demonstrating that the introduced hydrocarbon (ethanol) limited oxidation of the terminal Si surface. Further adjustment in the water/hydrocarbon ratio could achieve a balance point where carbon deposition and oxidation would balance each other.

5 As discussed above, exposure of carbon containing gases to high energy radiation can result in the formation of graphitic carbon films on surfaces, such as mirror surfaces, with detrimental effects to their reflectivity for EUV radiation. However, by the use of water vapor or oxygen in the disclosed process it is possible to remove graphitic carbon films. This is demonstrated in
10 the example below.

EXAMPLE 3

Referring now to Fig. 5, where it is shown that electron irradiation of adventitious hydrocarbon molecules present in a vacuum system can result in carbon deposition. Here, a 2kV electron beam, at a current density of about
15 $5\mu\text{A}/\text{mm}^2$, is incident onto a Si-terminated Mo/Si multilayer mirror. The mirror is maintained at a vacuum of about 5×10^{-10} Torr. As exposure to the incident electron beam increases, an increase in atomic percentage of carbon on the mirror surface takes place. After about 120 minutes of exposure, about 2×10^{-8} Torr of molecular oxygen is admitted to the vacuum chamber. At that time, the
20 increase in carbon deposition stops and no measurable additional carbon deposition occurs

Those skilled in the art will appreciate the importance of not adversely impacting the transmission of radiation, particularly for lithographic applications, by added gaseous components. The present invention provides an
25 important advantage in this regard since, as exemplified above, the partial

pressures of the various added gaseous molecular species need be only as high as necessary to affect surface chemistry. The use of gas pressures up to about 1×10^{-5} Torr would generally be adequate to provide a protective effect for most contamination problems while having negligible impact on lithographic throughput or uniformity. By way of example, the transmission of EUV radiation at 13.4 nm through 2 meters of a water/ethanol gas mixture, with each component at a partial pressure of about 1×10^{-5} Torr would be reduced by only about 0.05%.

In summary, the present invention provides a process for reducing or eliminating contamination and oxidation of surfaces caused by the interaction of high energy radiation on adventitious impurities. In particular, the process disclosed here can be used for reducing or eliminating oxide or carbon films on surfaces, such as the surface of silicon mirrors. Most particularly, the present invention provides special advantage in removing or reducing surface contamination in those components, such as masks and imaging optics, used in lithographic applications.

The above described method and the examples pertaining thereto are merely illustrative of applications of the principles of this invention and many other embodiments and modifications can be made by those of skill in the art without departing from the spirit and scope of the invention as defined in the claims.

CLAIMS

What is claimed:

1. A process for eliminating contamination of surfaces exposed to radiation,
5 comprising:

a) providing an enclosed space having a surface disposed therein, wherein
the atmosphere within the enclosed space contains contaminants;

b) introducing a gas capable of binding to the surface and reacting with
the atmospheric contaminants into the enclosed space; and

10 c) subjecting the contents of the enclosed space to extreme ultraviolet
radiation.

2. The process of claim 1, wherein the gas is comprised of hydrocarbon
molecules.

3. The process of claim 2, wherein the hydrocarbon molecules contain at least
15 one functionality selected from the group that includes ketones, aldehydes,
esters, alcohols, amines, thiols, and carboxylic acids.

4. The process of claim 3, wherein the gas comprises ethanol.

5. The process of claim 1, wherein the gas is water vapor or oxygen.

6. The process of any preceding claim, wherein the gas comprises a mixture of
20 gases.

7. The process of claim 6, wherein the mixture of gases is selected from the
group including a hydrocarbon gas, water vapor, and oxygen.

8. A process for eliminating contamination of lithographic surfaces,
comprising:

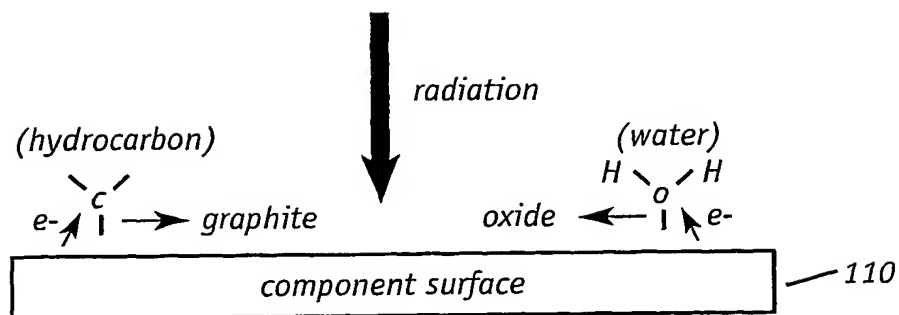
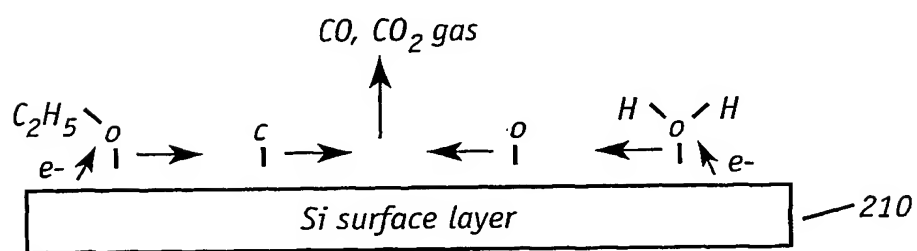
25 a) providing an enclosed space having at least one surface disposed
therein and wherein the enclosed space is at sub-atmospheric pressure and the
atmosphere within the enclosed space contains contaminants;

b) introducing a gas capable of binding to the surface and reacting with the atmospheric contaminants into the enclosed space; and

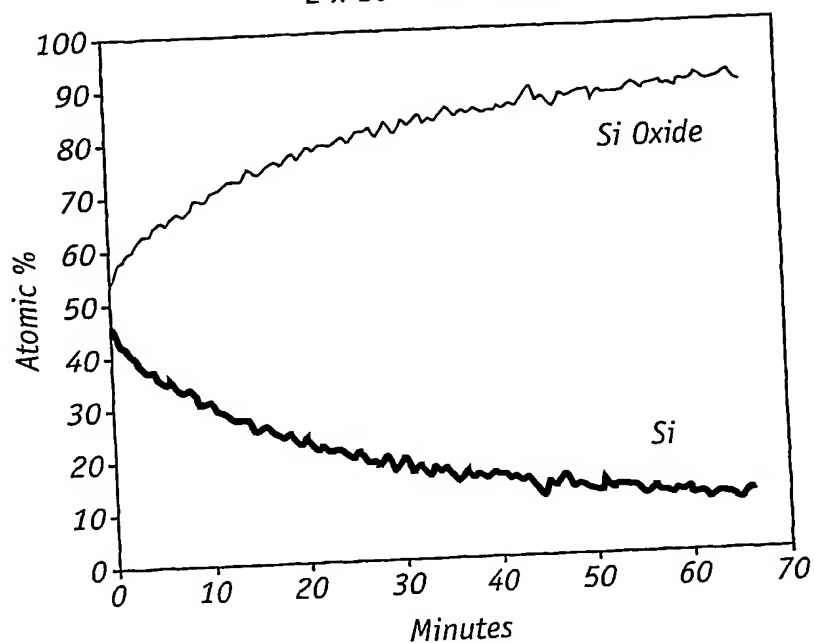
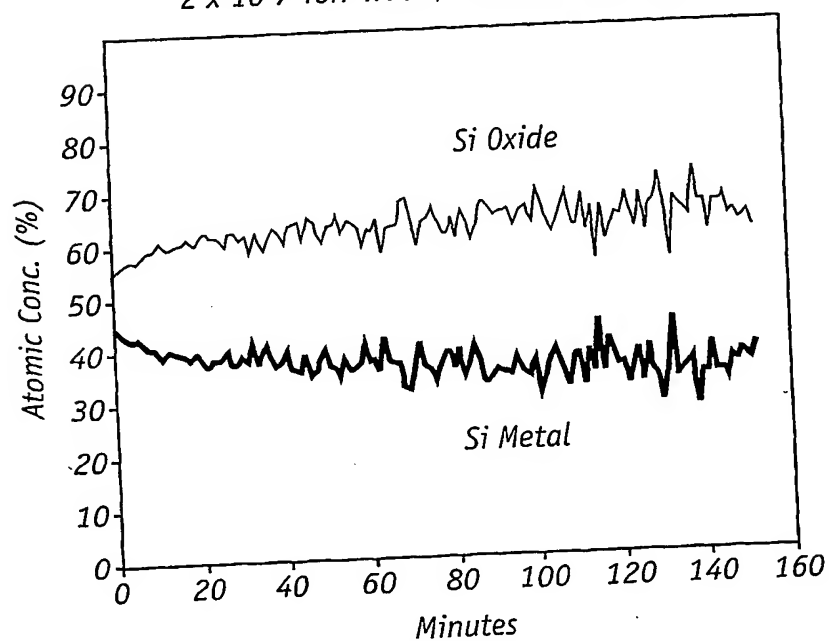
c) subjecting the contents of the enclosed space to extreme ultraviolet radiation.

- 5 9. The process of claim 8, wherein the gas is comprised of hydrocarbon molecules.
10. The process of claim 9, wherein the hydrocarbon molecules contain at least one functionality selected from the group that includes ketones, aldehydes, esters, alcohols, amines, thiols, and carboxylic acids.
- 10 11. The process of claim 10, wherein the gas comprises ethanol.
12. The process of claim 8, wherein the gas is water vapor or oxygen.
13. The process of any preceding claim, wherein the gas comprises a mixture of gases.
14. The process of claim 13, wherein the mixture of gases is selected from the
- 15 group including a hydrocarbon gas, water vapor, and oxygen.
15. The process of claim 8, wherein the partial pressure of the gas is less than about 10^{-5} Torr.

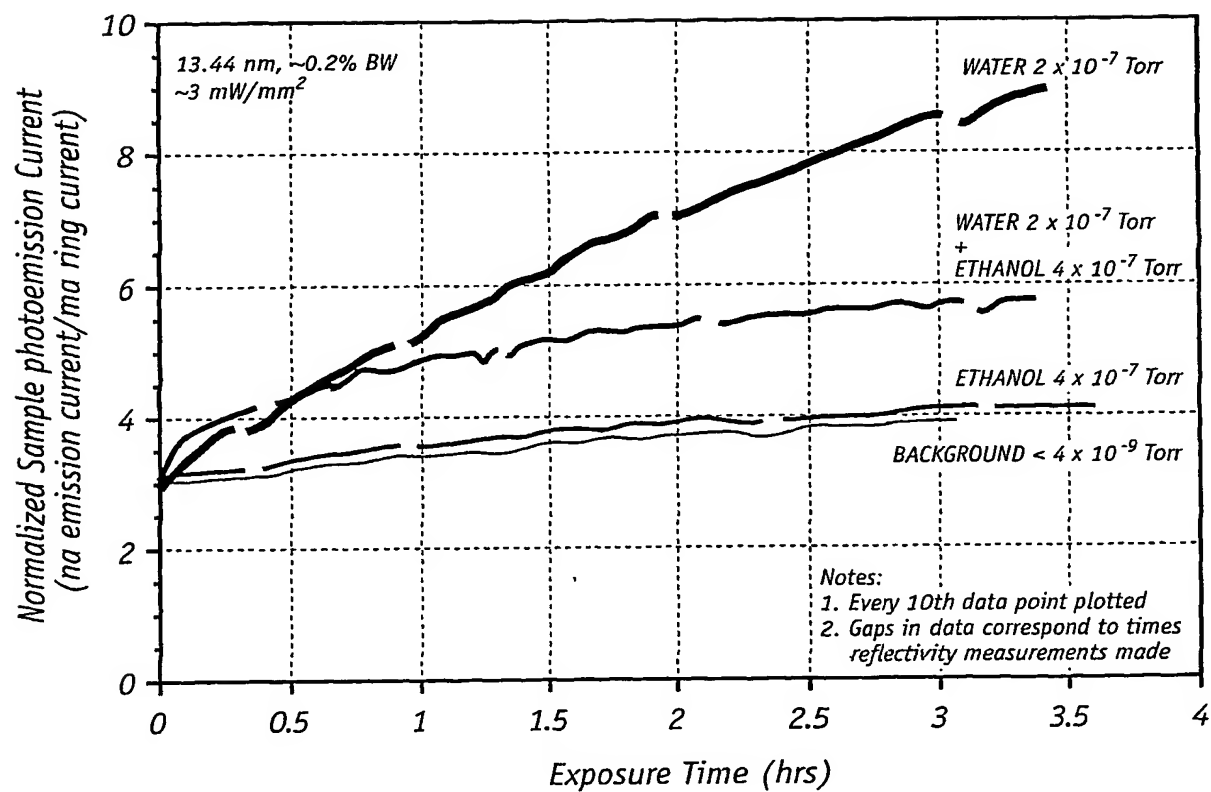
1/4

**FIG. 1****FIG. 2**

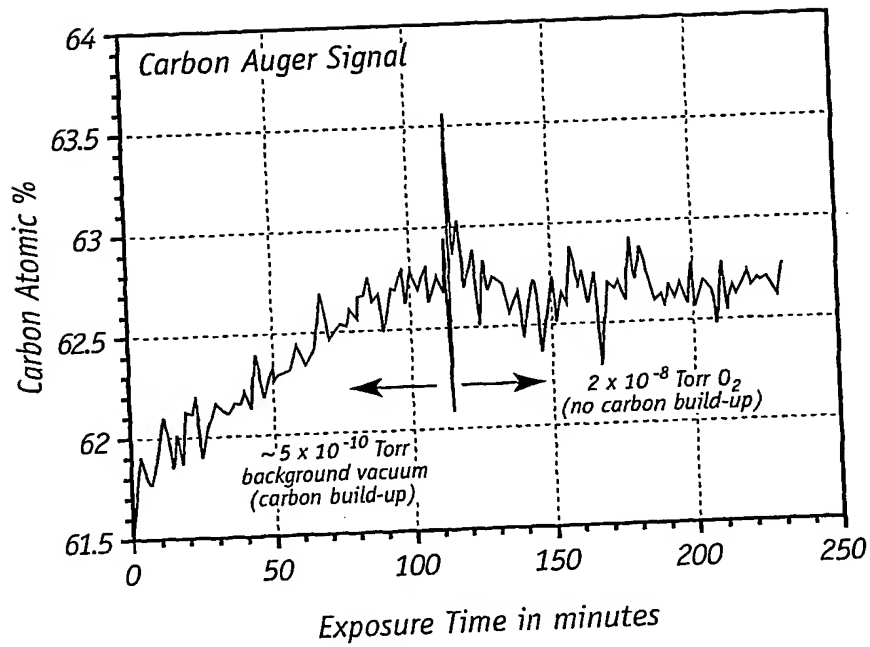
2/4

 2×10^{-7} Torr Water**FIG. 3A** 2×10^{-7} Torr Water, 4×10^{-7} Torr EtOH**FIG. 3B**

3/4

**FIG. 4**

4/4

**FIG. 5**

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/35394

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, IBM-TDB, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PRUETT C H: "Care and conditioning of optical surfaces for SRS beamlines" VACUUM DESIGN OF ADVANCED AND COMPACT SYNCHROTRON LIGHT SOURCES, UPTON, NY, USA, MAY 1988, no. 171, pages 167-174, XP008000138 AIP Conference Proceedings, 1988, USA ISSN: 0094-243X page 171 -page 173 ----	1,5-8, 12-15
E	US 6 252 648 B1 (HASE TOMOHARU ET AL) 26 June 2001 (2001-06-26) & JP-A-11224839 (published 17-08-1999) column 3, line 45 - line 53 column 5, line 4 - line 5 ----- -/--	1,5-8, 12-15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

31 January 2002

Date of mailing of the international search report

19/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Haenisch, U

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/35394

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>KUNZ R R ET AL: "Experimentation and modeling of organic photocontamination on lithographic optics"</p> <p>JOURNAL OF VACUUM SCIENCE & TECHNOLOGY B (MICROELECTRONICS AND NANOMETER STRUCTURES), MAY 2000, AIP FOR AMERICAN VACUUM SOC, USA, vol. 18, no. 3, pages 1306-1313, XP002188756</p> <p>ISSN: 0734-211X</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/35394

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6252648	B1	26-06-2001	JP 11224839 A	17-08-1999
			US 2001028447 A1	11-10-2001
<hr/>				